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## Hydrogen adsorption mechanism of MOF-74 metal–organic frameworks: an insight from first principles calculations

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The microscopic mechanism of the H<sub>2</sub> adsorption of two Mg-MOF-74 isoreticular frameworks, one with a benzenedicarboxylate (BDC) linker and the other with a dihydroxyfumarate (DHF) linker, were studied on the basis of density functional theory (DFT) method. Possible adsorption sites on the internal surface of the two MOFs were detected using *ab initio* molecular dynamics (AIMD) annealing simulations. The simulations were able to reproduce all adsorption sites which have been experimentally observed for the BDC-based M-MOF-74 frameworks with M = Ni and Zn. In descending order of binding strengths, they are the adsorption sites primarily induced by the open metal sites P<sub>1</sub>, the oxygen atoms of the oxido groups P<sub>2</sub> and the aromatic rings P<sub>3</sub>. The H<sub>2</sub>-framework binding strengths were properly evaluated by taking into account the vibrational zero-point energy (ZPE) contribution. An additional type of adsorption sites induced by the oxygen atoms of the carboxyl groups P<sub>4</sub> is predicted for the Mg-MOF-74 framework. Two types of adsorption sites primarily induced by the open metal sites P<sub>1</sub> and oxygen atoms of the carboxyl groups P<sub>2</sub> were predicted for the DHF-based Mg-MOF-74 framework. Detailed analysis of the electron density showed that the electrostatic interaction of the H<sub>2</sub> molecule with the charge distribution of the local framework environment within a radius of ~3.5 Å is a key factor to define adsorption positions and binding strength. The absence of the P<sub>4</sub> sites in the BDC-based Zn-MOF-74 framework is caused by the lower charge density at the oxygen atoms induced by less electro-positive metal. The substitution of the nonaromatic DHF linker for the aromatic BDC linker reduces the binding strength at the metal induced adsorption sites by 1.45 kJ mol<sup>-1</sup> due to the absence of the aromatic ring.

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### 1. Introduction

In recent decades, metal–organic frameworks (MOFs) have emerged as an advanced generation of nanoporous materials.<sup>1–3</sup> They have crystalline structures that are composed of metal clusters linked to each other by organic molecules to form

coordination networks. The large variation in chemical compositions and conformations of both metal-cluster nodes and organic linkers allows a great flexibility in designing and adjusting MOFs to achieve desired internal surface area, void volume as well as other physicochemical properties.<sup>2</sup> Consequently, designing MOFs for a wide range of applications such as catalysis,<sup>4</sup> gas storage,<sup>5</sup> gas sensors,<sup>6</sup> and biomedicine<sup>7</sup> etc. is a very active research area.

Numerous research studies have been devoted to designing MOFs for solid-state hydrogen storage applications.<sup>8,9</sup> One of the big challenges is the weak interaction between non-polar covalent hydrogen molecules and MOFs which typically can maintain high hydrogen uptake only at extreme conditions of low temperature and high pressure.<sup>8</sup> Using Grand Canonical Monte Carlo (GCMC) simulations of hydrogen adsorption in the IRMOF series, Frost and Snurr suggested that a reasonable H<sub>2</sub> uptake at ambient condition could be obtained with an isosteric heat of adsorption of 15 kJ mol<sup>-1</sup> (0.155 eV).<sup>10</sup> Particular interests have been paid for MOFs with open metal sites which can attract H<sub>2</sub> molecules *via* stronger electrostatic interactions. For example, the low loading heat of adsorption in Co-based SNU-15

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MOF with open Co(II) sites is up to 15 kJ mol<sup>-1</sup>.<sup>11</sup> However, its hydrogen uptake at  $T = 77$  K and  $P = 1$  bar is very low 0.74 wt% due to the low metal site density 0.0012 sites per Å<sup>3</sup>.

Considerable attention has been paid for MOF-74 series since they have higher open metal site density 0.0045 sites per Å<sup>3</sup> which corresponds to hydrogen uptake 2.5 wt% at  $T = 77$  K and  $P = 1$  bar.<sup>12-15</sup> The experimental values of low loading heat of H<sub>2</sub> adsorption of these materials are between 8 and 13 kJ mol<sup>-1</sup>.<sup>13</sup> GCMC simulations using classical force field demonstrated that the primary adsorption sites which are responsible for such loading heat of adsorption are induced by the electrostatic interaction between the positively charged open metal sites and the induced dipole moment of H<sub>2</sub> molecules.<sup>12</sup> This interaction was demonstrated to be strongly correlated with the ionic charge and the polarizability of the metal. The role of the linker was also revealed with the combination of experimental measurements and theoretical calculations. Kapelewski *et al.* were able to increase the low loading heat of adsorption by 1.5 kJ mol<sup>-1</sup> with a substitution of the original linker 2,5-dioxido-1,4-benzenedicarboxylate (BDC) using an isomer 4,6-dioxido-1,3-benzenedicarboxylate (*m*BDC).<sup>16</sup> Their electronic structure calculations based on the density functional theory (DFT) suggest that the extra contribution of *m*BDC linker enhances the metal site-H<sub>2</sub> interaction. Moreover, the neutron powder diffraction (NPD) experiments evidence that the change from *para* (BDC linker) to *meta* (*m*BDC linker) configurations of the carboxylic acid functionalities and hydroxyl substituents of the linker lead to the change in secondary adsorption sites.<sup>16,17</sup> The hydrogen uptake of *m*BDC-Co/Ni-MOF-74 frameworks at  $P = 100$  bar,  $T = 25$  °C is up to 13 g L<sup>-1</sup> and 1.2 wt%, slightly higher than their BDC-based counterparts. These frameworks were believed to be among the best of hydrogen physisorptive adsorbents.<sup>17</sup> However, they are still much lower than the targets of the US Department of Energy for practical fuel cell which require a volumetric uptake at least 50 g L<sup>-1</sup> in the temperature range -40 ÷ 60 °C at maximum delivery pressure 12 bar.<sup>18</sup> Based on classical GCMC simulations, Witman and coworkers suggested

that substituting the aromatic linker with a shorter aliphatic linker, 2,3-dihydroxyfumarate (DHF) can strongly enhance the volumetric uptake owing to the higher open-metal site density.<sup>19</sup>

In order to improve MOFs for practical hydrogen storage applications, it is crucial to understand the underlying mechanism of the H<sub>2</sub> adsorption. Various adsorption sites on the internal surface of MOF-74 frameworks have been reported by experimental works.<sup>16,20,21</sup> However, previous theoretical calculations primarily focused on the role of the open metal sites.<sup>12,13</sup> In this work, basing on *ab initio* molecular dynamics (AIMD) simulations, all possible adsorption sites including both metal-induced and linker-induced sites were predicted for the original BDC-based Mg-MOF-74 framework and its isoreticular DHF-based framework. Detail electronic structure analysis demonstrates that changing the electro-positivity of the metal affects the stability of linker-induced adsorption sites whereas the linker substitution gives significant influences on the binding strength of metal-induced adsorption sites.

## 2. Computational details

The crystal structures of MOF-74 family are based on rhombohedral lattice (Fig. 1a and b). Both BDC- and DHF-based frameworks belong to  $R\bar{3}$  space group. Their crystal structures were fully optimized on the base of static DFT calculations. There are 3 equivalent 1-dimensional (1D) void channels along *c* direction within a unit cell of each framework. Thus, adsorption sites in one channel are assumed to be the same as those in the others so that we only need to probe one channel.

Molecular dynamics simulated annealing method has been adopted to locate minima of the potential energy surface of adsorption systems.<sup>22-24</sup> In this work, *n* hydrogen molecules were randomly put into one void channel with *n* = 12 for the DHF-based framework and 25 for the BDC-based framework. These systems are so-called framework-*n*H<sub>2</sub> systems. The total number of atoms in a unit cell is 132 in the case of the DHF-based framework-12H<sub>2</sub> system and 212 in the case of the

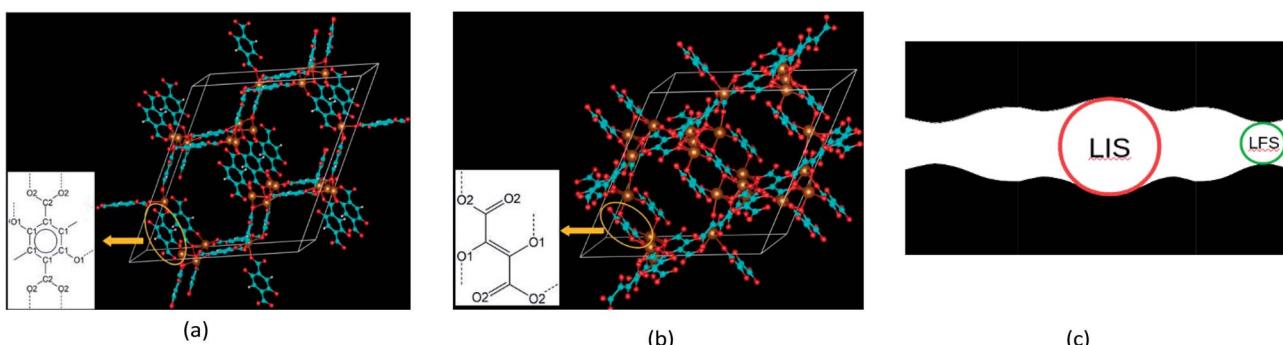


Fig. 1 (a) and (b) represent the crystal structures of the BDC-Mg-MOF-74 and DHF-Mg-MOF-74 frameworks, respectively. Red, brown, cyan and white spheres represent oxygen, magnesium, carbon and hydrogen atoms, respectively. The insets are schematic representations of corresponding linkers, i.e.  $(-\text{O}_2\text{C}_6\text{H}_2-\text{1,4-}(\text{COO})_2$  linker derived from 2,5-dioxido-1,4-benzenedicarboxylic acid (BDC) in (a) and  $(-\text{COO})_2\text{C}=\text{C}-\text{2,3-}(\text{O}-\text{O})_2$  linker derived from 2,3-dihydroxyfumaric acid (DHF) in (b). Dash lines in the insets denote dangling bonds which can be attached to metal atoms. The carbon atoms of the aromatic ring are labeled C1 and the carbon atoms of the carboxyl groups are labeled C2. The oxygen atoms of the oxido groups are labeled O1 and the oxygen atoms of the carboxyl groups are labeled O2. (c) A schematic representation of the largest included sphere (LIS) and the largest free sphere (LFS). The red circle, green circle and black shaded area denote the LIS, LFS and the space filled by the framework atoms, respectively.



BDC-based framework- $25\text{H}_2$  system. All framework- $n\text{H}_2$  systems were equilibrated at 300 K for 10 ps by AIMD simulations in NVT ensembles and then annealed from 300 K to 0 K for 10 ps. The  $\text{H}_2$  molecules were expected to reach various adsorption sites on the potential energy surfaces induced by the frameworks at the end of the annealing processes. In order to evaluate the influence of initial conditions on the annealing processes, three initial configurations sampled from 300 K NVT ensembles were considered.

The frameworks with a single  $\text{H}_2$  molecule at various adsorption sites, which are so-called single molecule adsorption models, were further optimized from the annealed structures with static DFT calculations. The electronic adsorption energies were estimated *via* the following formula:

$$\Delta E_i^0 = E_i^{\text{fr+gas}} - E^{\text{gas}} - E^{\text{fr}} \quad (1)$$

$E$  denotes total energy at  $T = 0$  K derived from static DFT calculations. The superscript 0 denotes the electronic contribution. The superscripts fr + gas, gas, and fr denote the single molecule adsorption system, one free gas molecule and bare framework respectively. Subscript "i" denotes type of adsorption site. The vibrational zero-point energy (ZPE) which purely originates from the quantum nuclear effect was taken into account for the total adsorption energy using the following formula:

$$\Delta E_i = (E_i^{\text{fr+gas}} + \text{ZPE}_i^{\text{fr+gas}}) - (E^{\text{gas}} + \text{ZPE}^{\text{gas}}) - (E^{\text{fr}} + \text{ZPE}^{\text{fr}}) \quad (2)$$

ZPE denotes the vibrational zero-point energy correction calculated using the following formula:<sup>25</sup>

$$\text{ZPE} = \sum_j \frac{h\nu_j}{2} \quad (3)$$

The sum is taken over all vibrational modes of the system,  $h$  is the Planck's constant and  $\nu_j$  is the frequency of the  $j$ th vibrational mode. The adsorption energies calculated using the single molecule adsorption model correspond to the zero loading adsorption energies.

First principles calculations were introduced within the framework of DFT implemented within the Vienna *ab initio* simulation package (VASP).<sup>26,27</sup> Exchange-correlation potentials

were expressed within the generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) functional.<sup>28</sup> The dispersion correction was added to original Kohn–Sham DFT equations in terms of atom-pairwise sum-over  $\text{C}_8\text{R}^{-8}$  potentials with cut-off distances and dispersion coefficients explicitly computed by S. Grimme *et al.* from first principles.<sup>29</sup> This method is commonly called DFT-D3. The valence electrons' wave functions, *i.e.* the wave functions of Mg 3s, C and O 2s, 2p and H 1s electrons were represented in plane wave basis set with cut-off energy of  $E_{\text{cut-off}} = 550$  eV. Highly oscillating core parts were simulated with projector augmented wave (PAW) method.<sup>30,31</sup> Since both BDC-based and DHF-based Mg-MOF-74 frameworks have large unit cells of sizes  $\sim 26.08 \times 26.08 \times 6.87 \text{ \AA}^3$  and  $\sim 18.76 \times 18.76 \times 6.87 \text{ \AA}^3$  respectively,<sup>19</sup> total energies were calculated on a  $\Gamma$ -center  $1 \times 1 \times 3$  Monkhorst–Pack mesh in reciprocal space. Both cut-off energy and  $k$ -mesh were chosen according to the convergence of the electronic adsorption energy of the strongest site within an error  $< 1$  meV per atom in comparison to the case using  $E_{\text{cut-off}} = 1000$  eV and  $k$ -mesh of  $4 \times 4 \times 12$ .

Self-consistent-field (SCF) convergence criterion for electronic structure optimization was  $10^{-6}$  eV. For crystal structural optimization, all atomic positions were relaxed until all atomic forces smaller than  $10^{-3}$  eV  $\text{\AA}^{-1}$ . The vibrational frequencies required for calculating ZPE corrections were obtained from normal mode analysis within harmonic approximation. The elements of the Hessian matrix were calculated from the DFT forces using finite difference method with the atomic step size 0.015  $\text{\AA}$ . The frequencies were then calculated as the square roots of the eigenvalues of the Hessian matrix. For reducing computational costs, only the vibrations of hydrogen molecules were considered. Benchmarks on two adsorption sites of two different types in DHF-based framework showed that the ZPE contributions of the framework to the adsorption energies are less than 2 meV.

AIMD simulations were carried out within the framework of Born–Oppenheimer approximation.<sup>32</sup> The temperature was controlled using Nosé–Hoover thermostat while the optimized volume of the unit cell of the frameworks were kept constant.<sup>33</sup> During the AIMD simulations, all displacements of the frameworks and gas molecules were allowed. The time step is 0.2 fs – 1/40 of the period of H–H stretching mode.

**Table 1** A summary of lattice parameters and porosity characteristics (accessible surface area (ASA), accessible volume (AV), largest included sphere (LIS) radius ( $R_I$ ) and largest free sphere (LFS) radius ( $R_F$ )) of the BDC-based and DHF-based Mg-MOF-74 frameworks

BDC-based Mg-MOF-74 framework			DHF-based Mg-MOF-74 framework	
	PBE-D3/plane wave + PAW (this work)	PBE/plane wave + PAW <sup>23</sup>	PND <sup>35</sup>	PBE-D3/plane wave + PAW (this work)
$a = b$ ( $\text{\AA}$ )	26.06	26.22	25.92 ( $T = 20$ K), 25.88 ( $T = 298$ K)	18.80
$c$ ( $\text{\AA}$ )	6.86	6.96	6.86 ( $T = 20$ K), 6.88 ( $T = 298$ K)	6.84
ASA ( $\text{m}^2 \text{ g}^{-1}$ )	1763	—	—	1042
AV ( $\text{cm}^3 \text{ g}^{-1}$ )	0.340	—	—	0.088
$R_I$ ( $\text{\AA}$ )	11.7	—	—	7.6
$R_F$ ( $\text{\AA}$ )	10.9	—	—	6.2



### 3. Results and discussion

#### 3.1. Crystal structure and porous geometry

The porosity characteristics including accessible surface area per gram (ASA), accessible volume per gram (AV), largest included sphere (LIS) radius ( $R_l$ ) and largest free sphere (LFS) radius ( $R_f$ ) were examined using Voronoi-mesh method with Zeo++ package.<sup>34</sup> A schematic representation of the LIS and the LFS is shown in Fig. 1c. In Table 1, calculated structure parameters and porosity characteristics of the two isoreticular Mg-MOF-74 frameworks are summarized and compared with those derived from powder neutron diffraction (PND) data<sup>35</sup> and previous PBE calculations using the same basis set and pseudopotential method.<sup>23</sup> According to this table, the dispersion correction is important to reproduce experimental lattice constants of the BDC-based framework. It should be noted that the NPD data show a contraction of the lattice constant  $a$  and

extension of the lattice constant  $c$  when the temperature increases from 20 K to  $\sim$ 470 K.<sup>35</sup>

The resulted unit cell volume change is a tiny oscillation  $\sim$ 0.09% around the average value  $\sim$ 3393 Å<sup>3</sup>. The lattice constant changes are also very small within this temperature range, *i.e.*  $<0.3\%$ . Hence, the optimized lattice unit cell can be used for the NVT AIMD simulation within the temperature range from 300 K down to 0 K.

There is no experimental data for the porosity characteristics except from the ASA which can be compared with Langmuir surface area calculated from the experimental N<sub>2</sub> adsorption isotherms. However, only experimental N<sub>2</sub> adsorption isotherms for the BDC-based Mn, Fe, Co and Ni-MOF-74 frameworks were reported with the deduced Langmuir surface areas 1797, 1535, 1432 and 1574 m<sup>2</sup> g<sup>-1</sup> respectively.<sup>16</sup> The theoretical ASA value for the BDC-based Mg-MOF-74 framework 1763 m<sup>2</sup> g<sup>-1</sup> is well within the experimental range. The shorter linker of the DHF-based framework lead to smaller lattice constant  $a$  ( $b$ ) and narrower void channel with smaller LIS and LFS radii but does not significantly change the lattice constant  $c$ . The narrower void channel, in turn, lead to the smaller ASA and AV. The ASA of the BDC-based framework is 1.69 times as large as that one of the DHF-based framework. Whereas the AV is 3.86 times larger accordingly.

#### 3.2. Annealing processes

Fig. 2 shows the annealed structures of framework- $n$ H<sub>2</sub> systems starting from three different initial configurations sampling within 300 K NVT ensembles. A general agreement between these annealing simulations is that there are five types of H<sub>2</sub> adsorption sites in the BDC-based framework and three types of adsorption sites in the DHF-based framework. In the Fig. 2, adsorption positions of the same type are represented by the same color of hydrogen atoms. Before going to analyse in detail of the adsorption positions, we first discuss the occupation temperature range within which H<sub>2</sub> molecules gradually occupy adsorption sites of each type. Table 2 is a summary of the occupation temperature ranges of various types with three different initial configurations. According to this, different initial configurations lead to a slight fluctuation  $\sim$ 5  $\div$  15 K of the occupation temperature range of each type. This fluctuation can be considered as a result of the thermal fluctuation of the

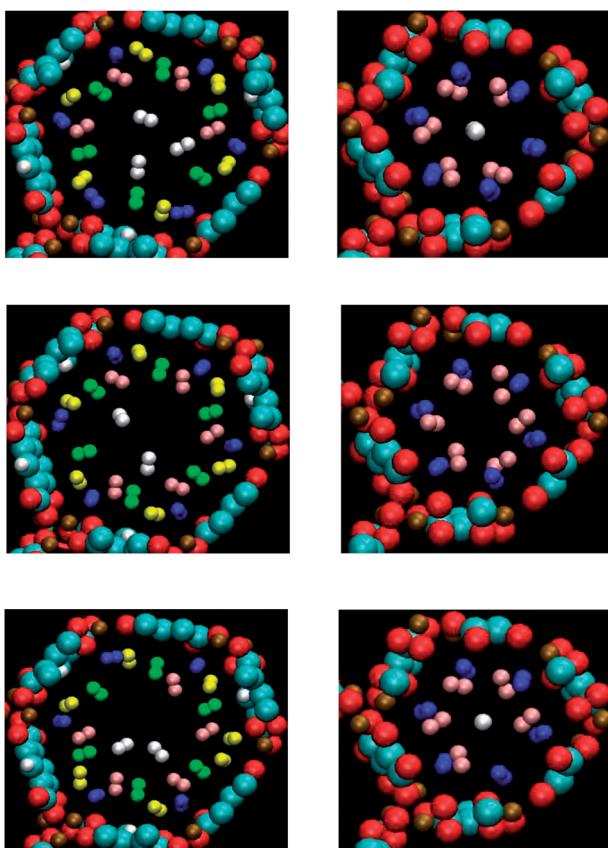


Fig. 2 Annealed structures of the BDC-based Mg-MOF-74-25H<sub>2</sub> system (on the left) and DHF-based Mg-MOF-74-12H<sub>2</sub> systems (on the right) starting from three different initial configurations sampling within the 300 K NVT ensemble. Red, brown, cyan and white spheres represent oxygen, magnesium, carbon and hydrogen atoms of the frameworks. Hydrogen atoms of the molecules adsorbed at P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub> and P<sub>5</sub> sites of the BDC-based framework are represented by blue, yellow, green, pink and white spheres respectively. Hydrogen atoms of the molecules adsorbed at P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> sites of the DHF-based framework are represented by blue, pink and white spheres respectively.

Table 2 A summary of adsorption temperature ranges in which various types of adsorption sites are populated during simulated annealing processes starting from 3 different initial configurations sampling from the 300 K NVT ensemble

	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>
BDC based	300–210 K	205–55 K	70–30 K	45–20 K	25–15 K
	300–215 K	220–55 K	85–30 K	55–20 K	30–20 K
	300–175 K	170–70 K	80–45 K	55–10 K	40–15 K
DHF based	300–170 K	260–50 K	50 K	—	
	300–210 K	155–65 K	—		
	300–210 K	150–20 K	20 K		



system during the annealing process. The initial configuration does not affect the occupation order between various types.

For the BDC-based MOF-25H<sub>2</sub> system, during the simulated annealing processes, the blue sites in Fig. 2, start to be occupied first, and then yellow sites, green sites, pink sites and white sites which are called P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub> and P<sub>5</sub> sites respectively. Due to the symmetry of honeycomb-like lattice, there are 6 sites of each type, and hence totally 30 adsorption sites, in one void channel of a  $R\bar{3}$  unit cell. The P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> sites have been experimentally found for the BDC-based Zn- and Ni-MOF-74 frameworks *via* NPD data.<sup>20,21</sup> Interestingly, the NPD experiments showed that these sites can be fully occupied in the BDC-based Zn-MOF-74 framework at  $T$  down to 30 K (ref. 20) which is the same as the lowest temperature for the P<sub>3</sub> sites to be fully occupied in our simulated annealing processes. The P<sub>5</sub> sites were coincidentally observed *via* the NPD experiments for the BDC-based Zn-MOF-74 framework at  $T = 15$  K. It should be noted that these sites were not experimentally observed for the Ni-based framework even at  $T = 4$  K because, in this case, the NPD data were collected at low loadings (0.5 and 1.5H<sub>2</sub>/Ni).<sup>21</sup> The P<sub>4</sub> sites were not experimentally observed for the BDC-based Zn-MOF-74 framework at loadings up to 4.2H<sub>2</sub>/Zn. The absence of P<sub>4</sub> sites in this framework will be discussed with the electronic structure analysis later. It should be noted that the number of H<sub>2</sub> molecules in the simulations, 25 molecules, is smaller than the total number of all adsorption sites, 30 sites. The first three types of adsorption sites have higher probability to be occupied so that they are fully occupied at the end of the annealing processes. The P<sub>4</sub> and P<sub>5</sub> sites are not fully occupied so the final temperatures of the corresponding occupation temperature ranges are the temperatures at which H<sub>2</sub> molecules populate P<sub>4</sub> and P<sub>5</sub> sites the last time.

For the DHF-based MOF-12H<sub>2</sub> system, the occupation order is the blue sites first, then yellow sites and white sites in the Fig. 2, mentioned as P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> sites respectively. The occupation temperature ranges of P<sub>1</sub> and P<sub>2</sub> sites shown in the Table 2 are similar to the P<sub>1</sub> and P<sub>2</sub> sites in the BDC-based framework, respectively. However, the dependence of the occupation temperature range of the P<sub>2</sub> sites on the initial configuration is stronger, denoting by a stronger thermal fluctuation  $\sim 100$  K. There are 6 P<sub>1</sub> and 6 P<sub>2</sub> sites but only one P<sub>3</sub> site, and hence 13 adsorption sites in one void channel of a unit cell while there are 12H<sub>2</sub> molecules. The P<sub>1</sub> sites are fully occupied first at temperature down to 170 K. In two of the simulated annealing processes, only 5 of 6 P<sub>2</sub> sites are occupied, the last H<sub>2</sub> molecule go to P<sub>3</sub> site instead of populating the last P<sub>2</sub> site. The P<sub>3</sub> site is occupied at the same time with the final occupation of P<sub>2</sub> sites at temperature down to 20 K.

In general, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub> sites of the BDC-based Mg-MOF-74 framework and P<sub>1</sub> and P<sub>2</sub> sites of the DHF-based framework are direct adsorption sites since they are directly attached to the frameworks. The P<sub>5</sub> sites of the BDC-based framework and P<sub>3</sub> sites of the DHF-based framework are indirect adsorption sites. In the following, direct adsorption sites will be discussed in detail to clarify the mechanism of the interaction between the frameworks and the H<sub>2</sub> molecules.

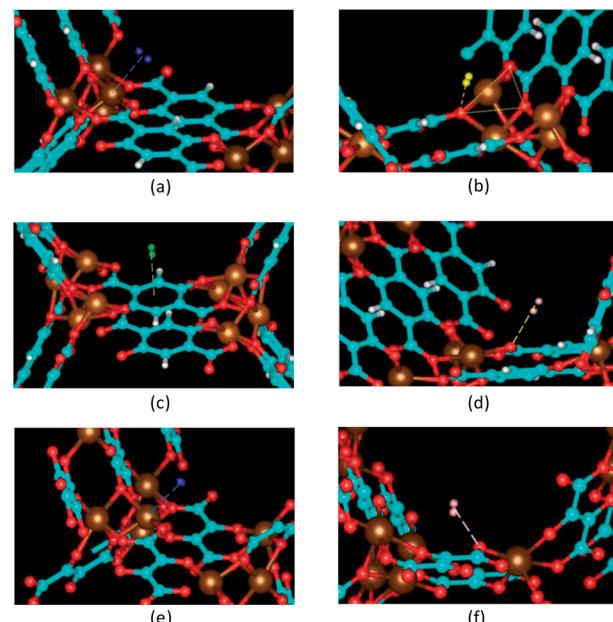


Fig. 3 Foreground illustrations of (a) P<sub>1</sub>, (b) P<sub>2</sub>, (c) P<sub>3</sub> and (d) P<sub>4</sub> adsorption positions in the BDC-Mg-MOF-74 framework. The P<sub>1</sub> and P<sub>2</sub> sites in the DHF-Mg-MOF-74 are illustrated in (e) and (f) respectively. Red, brown, cyan and white spheres represent oxygen, magnesium, carbon and hydrogen atoms of the framework respectively. P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub> hydrogen molecules in the BDC-based framework are represented by blue spheres in (a), yellow spheres in (b), green spheres in (c) and pink spheres in (d) respectively. P<sub>1</sub> and P<sub>2</sub> hydrogen molecules in the DHF-based framework are represented by blue spheres in (e) and pink spheres in (f) respectively. Dash lines denote the connection between the adsorbed H<sub>2</sub> molecules and the nearest framework atoms. Dot lines in (b) denote the oxygen triangle close to the P<sub>2</sub> site of the BDC-based Mg-MOF-74 framework.

### 3.3. Adsorption positions and binding mechanisms

**3.3.1. Adsorption positions.** Fig. 3 shows the optimized positions of a single H<sub>2</sub> molecule at various adsorption sites in the two Mg-MOF-74 isoreticular frameworks. A P<sub>1</sub> site of the DOBDC-based and DHF-based frameworks shown in Fig. 3a and e is the nearest to an open metal site with a distance 2.41 Å and 2.39 Å respectively. This distance is in good agreement with the experimental value 2.45 Å derived from the NPD data collected at 77 K for the DBC-based Mg-MOF-74 framework.<sup>36</sup> At this site, the H<sub>2</sub> molecule is likely in side-on position with respect to the Mg<sup>2+</sup> ion. The side-on position was shown to be common for a H<sub>2</sub> molecule when it is attached to an isolated positive ion.<sup>37</sup> Since the H<sub>2</sub> molecule has a quadrupole moment  $2.21 \times 10^{-40}$  C m<sup>2</sup>,<sup>38</sup> the side-on position with respect to the positive ion is to optimize the positive charge-quadrupole interaction. However, with the ligand environment of the MOF-74 frameworks, the hydrogen molecule is not exactly in ideal side-on position with equal Mg-H distances for two hydrogen atoms of the molecule. It slightly tilts, giving rise to the difference in Mg-H distances 0.01 Å in the case of the BDC-based framework and 0.02 Å in the case of the DHF-based framework.

A P<sub>2</sub> site of the BDC-based Mg-MOF-74 framework shown in Fig. 3b is located above a triangle of three oxygen atoms which



connect to the same metal ion, one from an oxido group called O1 and two from two carboxyl groups called O2 (see Fig. 1b). This site locates the nearest to O1 atoms with a distance 3.21 Å. The experimental values for this distance are 3.5 Å from the NPD data collected at 77 K.<sup>36</sup> At this site, the H<sub>2</sub> molecule is likely in head-on position with respect to the O1 atom. This is also the common position for a H<sub>2</sub> molecule when it is attached to an isolated negative ion in order to optimize the negative charge–quadrupole interaction.<sup>37</sup> The BDC ligand environment of the framework also gives rise to a slight tilt by an angle 6° from the ideal head-on position. A P<sub>2</sub> site of the DHF-based framework shown in Fig. 3f is the nearest to the oxygen atom of a carboxyl group O2 at a distance 2.47 Å. The H<sub>2</sub> molecule populate this site nearly at head-on position to the O2 atom with a significant tilting angle 22.5° induced by the DHF ligand environment.

A P<sub>3</sub> site of the BDC-based Mg-MOF-74 framework shown in Fig. 3c is above an aromatic ring of a linker at a distance 3.05 Å from the ring plane. This distance is in good agreement with the NPD value 3.08 Å for Co-based framework. It was shown that when a hydrogen molecule interacts with a molecule of a benzene dicarboxylic acid derivative, it prefers to bind head-on above the center of the aromatic ring at a distance ~3 Å with its axes perpendicular to the ring plane.<sup>37</sup> However, in the BDC-based framework, the H<sub>2</sub> molecule is significantly inclined by an angle of 25° with the normal of the ring plane denoting significant influence of metal cluster nodes on this linker-induced adsorption site. A P<sub>4</sub> site of the BDC-based Mg-MOF-74 framework shown in Fig. 3d is the nearest to the oxygen atoms of a carboxyl group O2 at a distance 3.01 Å. Similar to the P<sub>2</sub> site, the H<sub>2</sub> molecule is inclined by an angle of 6° from the ideal head-on position to the O2 atom because of the BDC ligand environment.

**3.3.2. Microscopic origin of the H<sub>2</sub> attractions.** The deformation of electron density upon adsorption at various sites at 0 K was calculated using the following formula:

$$\Delta\rho(\vec{r}) = \rho_{\text{framework}+\text{H}_2}(\vec{r}) - \rho_{\text{framework}}(\vec{r}) - \rho_{\text{H}_2}(\vec{r}) \quad (4)$$

$\rho$  denotes the electron density,  $\Delta\rho$  denotes the electron density deformation. The subscripts framework + H<sub>2</sub>, framework and H<sub>2</sub> denote the values of framework with one adsorption site occupied, bared framework and of an isolated hydrogen molecule respectively. Fig. 4 shows the iso-surfaces of the electron density deformation at isovalue 0.0001|e| Å<sup>-3</sup>.

For a P<sub>1</sub> site in both frameworks, the electron density is increased in an extended area on the Mg side of the H<sub>2</sub> molecule and decreased on the other side. This electron density deformation clearly evidences that the positive charge of the Mg<sup>2+</sup> cation polarizes the hydrogen molecule perpendicularly to its axis. Thus, the interaction of the Mg<sup>2+</sup> charge with the hydrogen induce-dipole is the dominating force to hold H<sub>2</sub> molecules at a P<sub>1</sub> site in both frameworks. Additionally, there are electron loss in the area between the oxygen and magnesium atoms, but the electron enhancements in the p-shaped area around the oxygen atoms and on the aromatic ring carbon atoms called C1 (see Fig. 1a). These atoms are located within a radius 3.5 Å (see Fig. 1a).

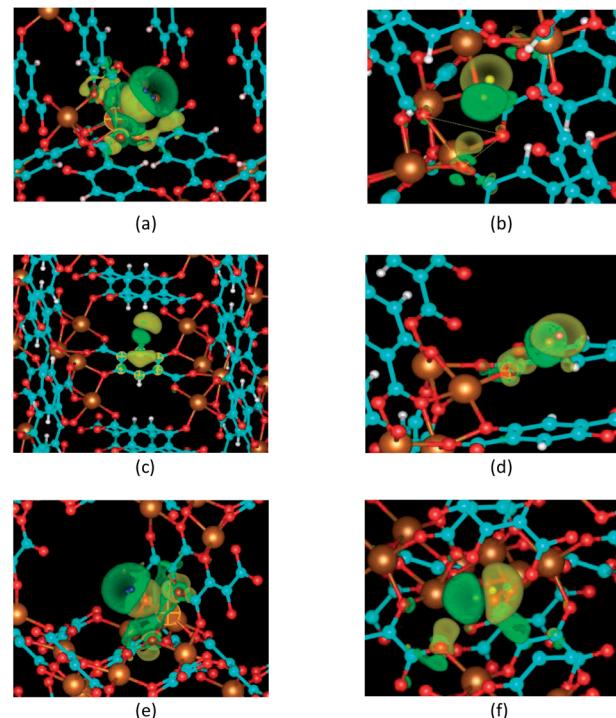


Fig. 4 Isosurfaces of the electron density deformations upon hydrogen adsorption onto (a) P<sub>1</sub>, (b) P<sub>2</sub>, (c) P<sub>3</sub> and (d) P<sub>4</sub> sites in the BDC-based Mg-MOF-74 framework, (e) P<sub>1</sub> and (f) P<sub>2</sub> sites in the DHF-based Mg-MOF-74 framework. The isovalue is 0.0001|e| Å<sup>-3</sup>. Yellow and green denote electron donated and loss surfaces respectively. Red, brown, cyan and white spheres represent oxygen, magnesium, carbon and hydrogen atoms of the frameworks respectively. P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub> hydrogen molecules in the BDC-based framework are represented by blue, yellow, green and pink spheres respectively. P<sub>1</sub> and P<sub>2</sub> hydrogen molecules in the DHF-based framework are represented by blue and pink spheres respectively.

around the P<sub>1</sub> site. This indicates remarkable contribution of the surrounding ligand environment within the radius 3.5 Å to the hydrogen attraction of the P<sub>1</sub> site.

The electron density deformations upon hydrogen adsorption to P<sub>2</sub> and P<sub>4</sub> sites in the BDC-based framework and a P<sub>2</sub> site in the DHF-based framework demonstrate the dominating role of the interaction between the H<sub>2</sub> induced-dipole and oxygen ions. The electron donated and loss regions on the two heads of the hydrogen molecule indicate a polarization of the hydrogen molecule along its axis. Obvious electron density deformations can be seen around the nearest framework atoms, *i.e.* O1 for the P<sub>2</sub> site, O2 for the P<sub>4</sub> site in the BDC-based framework and O2 for the P<sub>2</sub> site in the DHF-based framework. There are also other noticeable electron density deformation regions. For the P<sub>2</sub> site of the BDC-based framework, they are the regions around the two other oxygen atoms O2 of the oxygen triangle and the carbon atoms of the related carboxyl group C2 at distance. For the P<sub>4</sub> site of the BDC-based framework, they are the regions around the H atom of the aromatic ring. For the P<sub>2</sub> site of the DHF-based framework, they are the region between two carbon atoms within the radius 3.5 Å. These deformations indicate the contributions of the surrounding ligand environment within the radius 3.5 Å. The electron deformation upon the H<sub>2</sub>



**Table 3** A summary of noncorrected adsorption energies  $\Delta E^0$ , vibrational zero point energy corrections ZPE, ZPE corrected adsorption energies  $\Delta E$  at zero loading and noncorrected adsorption energies  $\Delta E_f^0$ , vibrational zero point energy corrections ZPE<sub>f</sub>, ZPE corrected adsorption energies  $\Delta E_f$  at full loading of the P<sub>1</sub> sites of direct adsorption sites in the BDC-based and DHF-based Mg-MOF-74 frameworks

BDC-based Mg-MOF-74 framework				DHF-based Mg-MOF-74 framework		
P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>1</sub>	P <sub>2</sub>	
$\Delta E^0$ (eV)	−0.192	−0.119	−0.105	−0.099	−0.183	−0.128
$\Delta E$ (eV)	−0.121	−0.088	−0.066	−0.062	−0.106	−0.080
ZPE (eV)	0.070	0.031	0.038	0.037	0.077	0.048
$\Delta E_f^0$ (eV)	−0.171	−0.110	−0.090	−0.074	—	—
$\Delta E_f$ (eV)	−0.100	−0.057	−0.042	−0.027	—	—
ZPE <sub>f</sub> (eV)	0.071	0.053	0.048	0.047	—	—

adsorption at a P<sub>3</sub> site in the BDC-based framework shows an electron donated region above the aromatic ring and a polarization of the H<sub>2</sub> molecule along its axis. This demonstrates the interaction between the H<sub>2</sub> induced dipole and the electron cloud of the ring at this site.

**3.3.3. The binding strength and the role of charge distribution.** Table 3 summarizes the electronic parts of the adsorption energies or the non-corrected adsorption energies  $\Delta E^0$ , ZPE corrections and ZPE corrected adsorption energies  $\Delta E$  of the direct adsorption sites. Negative values of adsorption energies mean that the bound states are more stable than unbound state. The contributions of vibrational ZPEs are positive, denoting a destabilization of the host-guest binding states. According to the adsorption energies, the descending order of binding strengths is P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub> in the BDC-based framework and P<sub>1</sub> and P<sub>2</sub> in the DHF-based framework. It consistently follows the order of occupation during the simulated annealing processes.

As discussed above, the electronic origin of the H<sub>2</sub> attraction is the electrostatic interaction between the H<sub>2</sub> molecule and the surrounding charged fragments of the MOF-74 frameworks within the radius  $\sim 3.5$  Å. Thus, charge distribution should be quantitatively considered to explain for the binding strength at various adsorption sites. The atomic charges were calculated from the DFT-derived charge density using Bader charge analysis method which defined atomic charge as total charge within

zero charge flux surface.<sup>39–42</sup> Table 4 show the calculated Bader atomic charges of the MOF-74 frameworks.

Both P<sub>1</sub> sites in the BDC- and DHF-based framework are primarily based on the interaction of the positive Mg ion and its surrounding oxygens with the H<sub>2</sub> molecule. As shown in Table 4, the Bader atomic charges of these ions are the same for both frameworks. However, the binding strength of a P<sub>1</sub> site in the DHF-based framework is smaller than in the BDC-based framework by 0.015 eV – 1.45 kJ mol<sup>−1</sup>. This difference can be assigned to the contribution of the aromatic ring in the BDC linker as denoted by the electron deformation on the ring, which is absent from the nonaromatic DHF linker. Similar linker-induced binding strength variation was also experimentally observed when the configuration of the BDC linker was changed from *para* to *meta* (mBDC linker). In this case, the extra contribution of the mBDC linker lead to an enhancement of the binding strength at the metal-induced site by 1.5 kJ mol<sup>−1</sup>.<sup>16</sup>

In the BDC-based Mg-MOF-74 framework, the Bader charge of oxygen ion in the oxido group O1 is slightly more negative than that of the oxygen ion in the carboxyl group O2 by 0.05|e| as seen in Table 4. However, the binding strength of the O1 induced adsorption site P<sub>2</sub> is significantly larger than the O2 induced adsorption site P<sub>4</sub>, 0.023 eV (2.22 kJ mol<sup>−1</sup>). This is due to the fact that, within the radius 3.5 Å, there are more framework atoms surrounding the P<sub>2</sub> site (one O1, two O2 and one C2 atom) than the P<sub>4</sub> site (only one O2 and one H atom). The Bader charge of the O2 ion in the DHF-based Mg-MOF-74 framework is the same as that of the O2 atom and less negative than that of the O1 atom in the BDC-based Mg-MOF-74 framework. However, the binding strength of the O2 induced site P<sub>2</sub> in the DHF-based framework is larger than the O2 induced site P<sub>4</sub> and very close to the O1 induced site P<sub>2</sub> in the BDC-based framework. The reason is that this site is also surrounded by more framework atoms (O2 and carbon atoms) than the O2 induced site P<sub>4</sub> in the BDC-based framework.

It is worth noting from experiments of H<sub>2</sub> adsorption in the BDC-based Mg-MOF-74 framework that the heat of adsorption depend on the loading rate.<sup>13</sup> The heat of adsorption at zero loading is a bit higher than at nonzero loading rate below 1H<sub>2</sub>/metal. In this loading rate range, the P<sub>1</sub> sites provide the main contribution to the hydrogen uptake.<sup>20,21</sup> The slight reduction of the heat of adsorption can be assigned to the site-site interaction. In the present work, the adsorption energy of each type of adsorption sites was calculated at zero loading and full loading rate of P<sub>1</sub> sites (1H<sub>2</sub>/metal). The absolute values of the ZPE corrected adsorption energy of a P<sub>1</sub> site at the zero loading and 1H<sub>2</sub>/metal loading in the BDC-based Mg-MOF-74 framework are

**Table 4** Atomic charges of metal and oxygen atoms in the MOF-74 frameworks derived from the DFT electron density by Bader charge analysis

BDC-based Mg-MOF-74 framework		DHF-based Mg-MOF-74 framework	BDC-based Zn-MOF-74 framework
Metal	+2 e	+2 e	+1.36 e
O1	$-1.93 \pm 0.02 e $	$-1.93 \pm 0.02 e $	$-1.19 \pm 0.02 e $
O2	$-1.88 \pm 0.01 e $	$-1.88 \pm 0.01 e $	$-1.16 \pm 0.01 e $



0.121 eV and 0.100 eV, respectively. These values are in good agreement with the experimental data of zero loading and low loading enthalpies of adsorption 0.119 eV and 0.109 eV.<sup>15</sup> At loading rate larger than 1H<sub>2</sub>/metal, the main contributions to the experimental enthalpies come from the P<sub>2</sub> and P<sub>3</sub> sites. The absolute values of the ZPE corrected adsorption energies of a P<sub>2</sub> and P<sub>3</sub> site at 1H<sub>2</sub>/metal loading are 0.057 eV and 0.042 eV respectively, which are around the experimental enthalpies of adsorption at loading rate >1H<sub>2</sub>/metal ~0.052 eV.

Concerning the absence of P<sub>4</sub> sites in the BDC-based Zn-MOF-74 framework suggested by the NPD experiment,<sup>20</sup> it is worth noting that the main origin of these sites is the O<sub>2</sub> negative charge. The more negative the O<sub>2</sub> ion is, the stronger the H<sub>2</sub> attraction is. On the other hand, Mg is more electro-positive than Zn so that the oxygen atoms surrounding Mg are expected to be more negatively charged than those surrounding Zn. The reducing in charge density at the O<sub>2</sub> site is expected to reduce the binding strength at the P<sub>4</sub> site or even destabilize this site. In this work, the charge distribution of the BDC-based Zn-MOF-74 was examined using DFT derived electron density and Bader charge analysis. The results are also shown in Table 4. It is clear that the charge of Mg ion in the Mg-MOF-74 framework is +2|e|, larger than that of Zn ion in the Zn-MOF-74 framework +1.36|e|. The ionic charges of neighbouring O<sub>2</sub> atoms are -1.9 and -1.2|e| in the Mg- and Zn-based framework respectively. The ZPE corrected adsorption energy of a P<sub>4</sub> site in the BDC-based Zn-MOF-74 was also calculated at zero loading and 1H<sub>2</sub>/metal loading. The zero loading value is -0.042 eV, 0.02 eV - 1.93 kJ mol<sup>-1</sup> weaker than the case of the Mg-MOF-74. At loading rate 1H<sub>2</sub>/metal, the adsorption energy of a P<sub>4</sub> site is -0.027 eV and -0.007 eV for Mg- and Zn-MOF-74 framework, respectively. The predicted smaller values of the adsorption energy of the P<sub>4</sub> site agree with the fact that it has been absent in the Zn-based framework. However, due to the higher adsorption energy it would be interesting to check experimentally whether the H<sub>2</sub> molecules could be occupied at the P<sub>4</sub> sites in Mg-based framework.

The electronic adsorption energy at the ring induced site P<sub>3</sub> in the BDC-based MOF-74 framework is 0.105 eV (10.13 kJ mol<sup>-1</sup>), higher than those of the BDC derivatives ~4 kJ mol<sup>-1</sup>.<sup>37</sup> The ZPE corrected adsorption energy of this site is -0.066 eV (6.37 kJ mol<sup>-1</sup>), stronger than that of the ring site in the MOF-5 framework 5.1 kJ mol<sup>-1</sup>.<sup>22</sup> The enhancement of the binding strength between the ring and the H<sub>2</sub> molecule in the MOF-74 can be explained basing on the fact that adding electron-donated substituents such as -OH, -CH<sub>3</sub>, -NH<sub>2</sub> can increase the binding strength.<sup>37</sup> In the case of MOF-74, the enhancement of H<sub>2</sub> attraction can come from the fact that there are two oxido substituents on the ring which directly connect to strong electron-donating metal atoms. Whereas, there is no such substituent on the BDC linker in the MOF-5.

## 4. Conclusions

In conclusion, the microscopic origin of H<sub>2</sub> adsorption onto the internal surface of the MOF-74 frameworks were explored

on the base of AIMD simulations and DFT electronic structure calculations. The guest molecules show significant electrostatic interactions with the local framework environment within a radius 3.5 Å. Four types of direct adsorption sites on the internal surface of the BDC-based Mg-MOF-74 framework were specified. With shorter nonaromatic linker, the DHF-based MOF-74 framework provides only two types of direct adsorption sites. The primary adsorption sites P<sub>1</sub> in both frameworks are due to the interaction of the H<sub>2</sub> molecules with the positively charged open metal sites and their surrounding oxygen sites. In the case of the aromatic BDC linker, the contribution of the high electron density aromatic rings within the distance 3.5 Å from these sites enhances the binding strength by 1.45 kJ mol<sup>-1</sup> in comparison to the case of nonaromatic DHF linker. The secondary adsorption sites originate from the interactions of the H<sub>2</sub> molecule with the negatively charged oxygen sites and the high density electron clouds of the aromatic rings. The reduction of the electropositivity of the metal can induce reductions of the negative charges of the oxygen sites which in turn destabilize the oxygen induced adsorption sites.

## Conflicts of interest

There are no conflicts to declare.

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